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ELECTRICAL AND THERMOELECTRICAL PROPERTIES OF SOME NEW CONJUGATED POLYMERS IN THIN FILMS

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The temperature dependences of the electrical conductivity and Seebeck coefficient for some polymers with pyrimidine repeating units are studied using thin films samples deposited from solutions. It was found that the polymers show semiconducting properties. The mechanism of electrical conduction in respective polymers is discussed. Some correlations between molecular structure of polymers and their semiconducting characteristics are established.

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1. Introduction

The theoretical and experimental studies on the electrical conduction mechanism in organic semiconductors, especially in organic semiconducting polymers, has attracted the attention of a large number of investigators in the last two decades [1, 2].

The growing interest for this topic is strongly stimulated by the role of these materials in many domains of solid-state device technology (sensors, photodetectors, organic solar cells, thin-film transistors, etc) [3, 4].

The mechanism of electrical conduction in semiconducting organic polymers having a complex molecular structure is, in present, far from being fully understood. Generally, the obtained experimental results for different polymers have been interpreted in terms of various conduction mechanism, such as band conduction, variable hopping conduction, etc. [2, 4, 5].

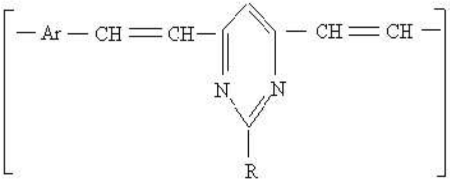
In a series of previous papers [4-7], we have investigated the temperature dependence of electrical conductivity and Seebeck coefficient of some organic compounds which showed typical semiconducting characteristics.

This paper reports the electrical properties of some polymers with pyrimidine repeating units in thin films. The investigated polymers show semiconducting properties. Some correlations between these properties and molecular structure of the polymers have been established.

2. Experimental

The studied polymers, poly-4-vinylene-6-arylenevinylene-pyrimidines, were prepared according to the ability of the N-vicinal pyrimidinic methyl groups in 4,6-dimethyl-pyrimidine and 2-phenyl-4,6-dimethylpyrimidine to react with various aromatic diadelhydes [8, 9].

The respective polymers obey the following general formula:



where substitutes R and Ar are listed in Table 1.

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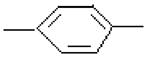
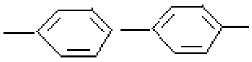
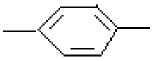
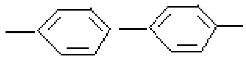
Table 1. Substitutes R and Ar from the general formula of the studied polymers

Polymers	R	Ar
PPRU.1	- H	
PPRU.2	- H	
PPRU.3	- C_6H_5	
PPRU.4	- C_6H_5	

The preparation method of the polymers and some of their physical and chemical properties are described in [8, 9].

The electrical properties of mentioned polymers were investigated on the thin-film samples deposited from solution, the solvent being dimethylformamide. Glass substrates were used. The experimental conditions have been established in order to obtain samples of compact structure and uniform thickness over sufficiently large areas of the substrate surface [4, 6, 10, 11].

The sandwich type cells have been used for the study of current-voltage characteristics [12].

The thickness of polymeric films was determinated by Fizeau’s method for fringers of equal thickness [13]. The obtain values for investigated polymeric films ranged between 0.37 μm and 3.15 μm. The thickness of thin – film electrodes was about 2.5 μm. In the case of sandwich-type cells, the contacted area of the polymeric films with electrodes was 4 mm^2 [20].

The experimental arrangement used for the study of temperature dependence of the electrical conductivity was similar to that described in [10, 11].

The Seebeck voltage is given by [4, 14]:

$$V_s = \alpha(T)\,\Delta T \tag{1}$$

where $\alpha(T)$ is the Seebeck coefficient at temperature T.

In our experiments, the temperature difference, $\Delta T = T_2 - T_1$, was 8-10 K and α is admitted to correspond to the temperature $T = (T_1+T_2)/2$. The Seebeck coefficient was measured by using sonde-electrode method [4, 5]. The Seebeck voltage was determinated by using a standard d.c. potentiometric method.

The measurements of electrical parameters (electrical resistivity, Seebeck voltage, etc.) were performed using a Keithley 6517 electrometer and a Keithley 2010 multimeter.

3. Results and discussion

For investigated polymers, it was experimentally established that the thin films with stable structure and reproducible electrical properties can be obtained if, after preparation, they are submitted to a heat treatment. This consists of several successive heatings and coolings (usually 2 to 5 cycles) within a certain temperature range, ΔT, characteristic for each polymer (Table 2).

After the treatment, the temperature dependences of the electrical conductivity and Seebeck coefficients become reversible.

The study of the temperature dependence of the electrical conductivity during this heat treatment may provide very interesting information on the processes taking place in the investigated samples [4, 10, 11].

In Fig. 1 is presented the typical shape of the $\ln\sigma = f(10^3/T)$ curves during the heat treatment for one of the investigated samples. At the first heating, a decrease of the electrical conductivity with increasing temperature is observed, within the lower temperature range. This behaviour is probably due to the removal of some impurities (adsorbed and/or absorbed gases, residual solvent molecules, etc) from the sample. Structural changes in the studied films may also occur during the heat treatment [4, 5, 11]. In the higher temperature range, the $\ln\sigma = f(10^3/T)$ curve shows an exponential increase of the electrical conductivity with temperature. For the first cooling, the $\ln\sigma = f(10^3/T)$

dependence is typical for semiconducting materials. By carrying further the heat treatment, $\ln\sigma = f(10^3/T)$ curves, similar to those of the first cooling, are obtained. A detailed analysis of these dependences, for a great number of organic semiconductors, is presented in a series of our previous paper [5, 11].

For heat-treated samples, an exponential increase of the electrical conductivity with temperature has been observed in all temperature range, ΔT (Fig. 2).

It can be observed that all these curves present two distinct parts with different slopes: a portion with a smaller slope, where probably the extrinsic conduction prevails and a portion with a larger slope corresponding to an intrinsic conduction.

In our previous papers, for a large number of polymers with a similar molecular structure, we found that at higher temperature ranges (T>330K) the temperature dependence of the electrical conductivity, σ, obeys the well known exponential law [14-16].

$$\sigma = \sigma_0 \exp(-\Delta E/2kT) \tag{2}$$

where σ_0 is a parameter depending on the semiconductor nature, ΔE denotes the thermal activation energy of electrical conduction (energy gap in model based on band structure representation), and k is Boltzmann's constant.

Based on the Eq. (2), the values of ΔE were calculated from $\ln\sigma = f(10^3/T)$ curves within the intrinsic domain. In Table 2 are listed these values obtained for eight samples of studied polymers.

It can been observed that the respective values depend on the molecular structures of the polymers. The lowest activation energies were found for the polymers PPRU.1 and PPRU.3 containing o-phenilic structure insertions. The substitution of ($-C_6H_4-$) group with ($-C_6H_4$) - (C_6H_4-) determines a decrease of electrical conductivity and an increase of activation energy. These facts indicate a decrease of conjugation system for polymers PPRU.2 and PPRU.4.

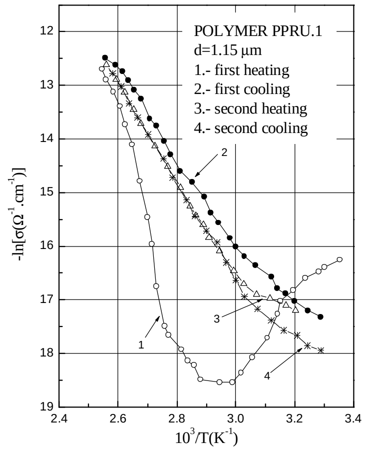


Fig. 1. Temperature dependence of the electrical conductivity during heat treatment

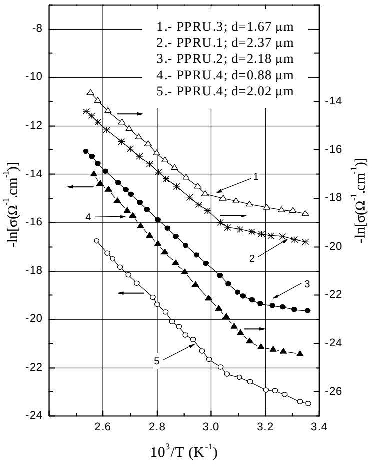


Fig. 2. Temperature dependence of the electrical conductivity of heat-treated samples

Gutman, Lyons, Eley and others [15, 16] have considered that $\ln\sigma_0$ linearly depends on ΔE:

$$\ln\sigma_0 = \alpha\,\Delta E + \beta \tag{3}$$

where α and β depend on the individual classes of compounds with similar structure.

The expression is verified by our experimental results (Fig. 3). For the class of studied polymers, the parameters α and β, calculated from $\ln\sigma_0 = f(\Delta E)$ dependence, have the following values: $\alpha = 21.43\ \mathrm{eV}^{-1}$ and $\beta = -25.23$.

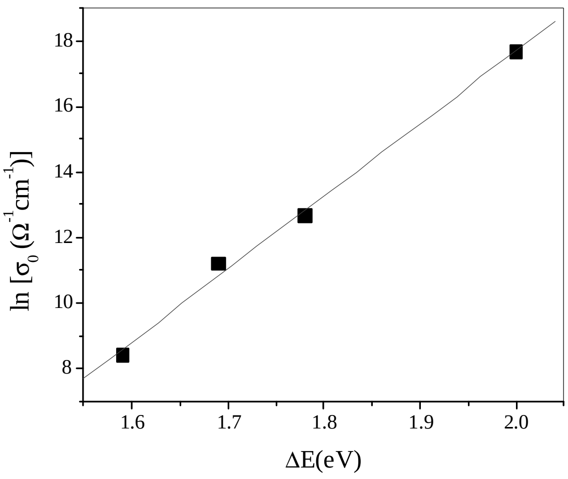


Fig.3. The dependence of $\ln\sigma_0$ on ΔE.

Table 2. Values of some characteristic parameters of studied samples Film thickness (d), electrical conductivity at room temperature before heat treatment (σ_c), temperature range in which the heat treatment of the sample was performed (ΔT), electrical conductivity at room temperature after heat treatment (σ_T), characteristic temperature for heat-treated sample (T_C), activation energy of electrical conduction in extrinsic and intrinsic domains, respectively (ΔE_{ex} and ΔE).

Polymer	d (μm)	σ_c ($\Omega^{-1}cm^{-1}$)	ΔT(K)	σ_T ($\Omega^{-1}cm^{-1}$)	T_C (K)	ΔE_{ex} (eV)	ΔE (eV)
PPRU.1	1.15	8.85×10^{-8}	295-395	1.68×10^{-8}	328	0.52	1.60
PPRU.1	2.37	1.95×10^{-8}	300-393	2.52×10^{-8}	325	0.34	1.58
PPRU.2	1.09	2.05×10^{-9}	294-390	2.38×10^{-10}	323	0.43	1.77
PPRU.2	2.18	1.14×10^{-8}	295-392	3.07×10^{-9}	320	0.30	1.80
PPRU.3	0.93	7.67×10^{-9}	300-390	1.04×10^{-9}	335	0.35	1.70
PPRU.3	1.67	5.12×10^{-8}	300-390	8.36×10^{-9}	336	0.38	1.68
PPRU.4	0.88	2.15×10^{-10}	295-385	2.29×0^{-11}	320	0.45	2.00
PPRU.4	2.02	8.50×10^{-10}	298-385	6.22×10^{-11}	330	0.73	1.95

The sign of the Seebeck coefficient, α, was negative for all investigated samples, indicating the predominance of the electrons as majority charge carriers.

Fig. 4 shows typical dependences $\alpha = f(10^3/T)$ for investigated polymers. It can be observed that Seebeck coefficient decreases with increasing temperature within the intrinsic conduction domain.

By assuming that the band–conduction model is a suitable model which explains the carrier transfer in the studied polymers, some values of the characteristic parameters of respective polymers could be calculated based on the $\ln\sigma = f(10^3/T)$ and $\alpha = f(10^3/T)$ dependences. The methods for determination of corresponding parameters are described in detail in [4,5,11].

The scalar effective mass of the charge carriers has been determined using static current-voltage characteristics for thin-films sandwich systems of the metal/organic polymer/metal type [12].

The rate of carrier mobilities, b, ($b = \mu_e / \mu_g$, where μ_e denotes the electron mobility and μ_g is the hole mobility) can be determined by means of the following relationship [4,11,14]:

$$b = [\Delta E/2 \cdot \Delta(1/T) - |e| \cdot \Delta\alpha] \cdot [\Delta E/2 \cdot \Delta(1/T) + |e| \cdot \Delta\alpha]^{-1} \tag{4}$$

where $\Delta\alpha$ is the variation of the Seebeck coefficient corresponding to a determinated variation $\Delta(1/T)$ of the temperature.

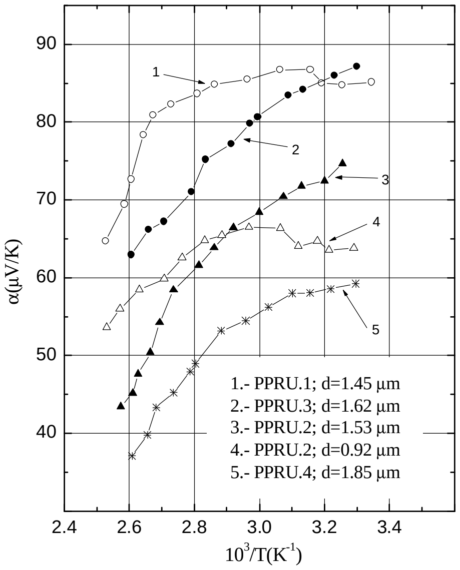


Fig. 4. The dependences $\alpha=f(10^3/T)$ for the investigated samples .

The obtained values for mentioned parameters are listed in Tables 2 and 3. It can observed that the values of b little differ from unity.

Table 3. Values of some characteristic parameters of investigated samples: film thickness (d), energy gap (ΔE), ratio of carrier mobilities (b), carrier concentrations at 350 °C (n_i).

Polymer	d(μm)	ΔE(eV)	b	$n_i(cm^{-3})$
PPRU.1	1.45	1.60	1.67	1.34×10^{21}
PPRU.2	1.53	1.78	1.68	9.90×10^{19}
PPRU.2	0.92	1.80	1.25	7.40×10^{19}
PPRU.3	1.62	1.68	1.13	7.62×10^{19}
PPRU.4	1.85	2.00	1.10	4.07×10^{19}

4. Conclusions

The temperature dependences of the electrical conductivity, σ, and Seebeck coefficient, α, were studied for four polymers with pyrimidine repeating units. The measurements were performed using thin-film samples deposited from solutions. The investigated polymers have typical semiconducting characteristics. The analysis of $\ln\sigma = f(10^3/T)$ and $\alpha = f(10^3/T)$ dependences, show that the model based on the band-gap representation could be suitable in the study of the electron transport mechanism through investigated polymers.

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